

Cryogenic Liquids: The Invisible Danger

By Lieutenant John C. Berna

Incident #1—FDNY units responded to a call for a leaking carbon dioxide cylinder in the basement of a McDonald's restaurant. As they entered the basement, the three members investigating began to get light-headed and dizzy. They sensed that something was wrong, immediately donned their facepieces and continued investigative efforts.

Incident #2—Workers self-evacuated a basement after liquid carbon dioxide was delivered to a restaurant. They complained of feeling faint and sick. The Fire Department was called as the delivery driver left the scene, unaware of what just occurred. On arrival, FDNY members evacuated customers from the first floor. As members entered the basement, they, too, began to feel the effects of an oxygen-deficient atmosphere. They evacuated and waited the arrival of a Haz-Mat Technician Unit. The oxygen reading in the room where the tank was located was as low as 10 percent. Had anyone entered the room without respiratory protection, a few breaths and he/she would have been rendered unconscious.

Incident #3—While an employee was filling a cryogenic Dewar at a Manhattan health spa, the vessel overfilled, causing liquid nitrogen to spill out, freezing the top of the cylinder and frosting the floor and wall. FDNY Firefighters arrived and attempted to shut down the tank, at which point, the valve hand wheel snapped off at the stem. Luckily, the valve was completely closed by that time. Oxygen readings in the therapy room were at 18 percent. Ironically, the very next day, at the same location (and in the same room), the exact same incident occurred again. Oxygen readings were at 12 percent. If responders were not wearing respiratory protection, after just a few breaths, they would have had to be assisted by others in order to leave the oxygen-deficient atmosphere.

What these three recent incidents have in common is that the products leaking from these cylinders were cryogenic liquids, stored in a DOT 4L cryogenic tank or Dewar. Initial responders also learned, in many cases very quickly, that the danger was invisible and nothing seemed out of the ordinary.

Cryogenics

In today's society, we produce, ship, store and use cryogenic liquids more than ever before. There are applications for use in both commercial and industrial settings. In physics, a cryogenic is defined as a gas that can be liquefied at a temperature of -240 degrees Fahrenheit or below. The fire service recognizes the U.S. Department of Transportation's (DOT) definition of a cryogenic as "a liquid with a boiling point below -130 degrees Fahrenheit." No matter which definition we use, we're talking about very cold substances. They are cold enough to cause permanent damage to your eyes and freeze your skin without you feeling any pain—initially. No worries, the pain will come once the exposed skin begins to thaw. The properties of cryogenics stored at such cold temperatures create three major dangers with which responders must be aware.

The Three Dangers

1. **Asphyxiation**—When these liquids escape their container, they immediately vaporize (turn into a gas) and displace the surrounding air. This is a common problem faced by initial first responders. The creation of an oxygen-deficient atmosphere causes asphyxiation in humans. There may be no way to tell whether a leak has occurred and none of our senses may alert us to danger. The only way to confirm an oxygen-deficient (or -enriched) atmosphere is the oxygen sensor on our meters. The biggest misconception of an oxygen-deficient/-enriched atmosphere caused by a cryogenic liquid leak is that it is always accompanied by the presence of a vapor cloud; this is absolutely



Photo 1—A DOT 4L cryogenic cylinder.

false. A vapor cloud may be non-existent, deficient or enriched far beyond the cloud area if one is visible.

Air normally is 21 percent oxygen by volume. A level of 19.5 percent or below is considered an oxygen-deficient atmosphere, while a level of 23 percent or greater is an oxygen-enriched atmosphere. Reducing the oxygen concentration to 15 to 16 percent induces symptoms of asphyxiation. Early signs of asphyxiation include light-headedness, dizziness, giddiness, mental confusion, loss of coordination, nausea, weakness and fainting.

Two facts that should be understood by all first responders is that exposure to atmospheres containing 12 percent or less oxygen leads to rapid unconsciousness, possibly without any warning. This can occur if the condition is reached by an immediate change of environment or through gradual depletion of oxygen over time. Secondly, meter readings of oxygen higher than 19.5 percent do not always indicate a safe environment. Either way, you *must* wear your facepiece.

As a side note, there is an exception—liquid oxygen—which has an expansion ratio of 1:860. When you have a liquid oxygen leak, you do not produce an oxygen-deficient atmosphere, but rather an enriched atmosphere, which allows things to burn faster and hotter.

2. **Extreme Cold**—Think about the boiling point of water. It will



Photo 2—Valves, gauges and relief devices of a DOT 4L cylinder.

Commonly Encountered Cryogenic Liquids

Listed below are the more commonly encountered cryogenic liquids, their expansion ratios, uses and associated hazards.

Oxygen—1:860. Oxygen is the only cryogenic liquid that will produce an oxygen-enriched atmosphere. It is placarded as an oxidizer, which supports combustion. It is slightly heavier than air and most commonly is found in hospital and medical facility settings. Incompatibilities include oils, grease and hydrocarbon fuels, which, when mixed, can cause an explosive atmosphere.

Nitrogen—1:696. Nitrogen is inert, colorless, odorless, non-corrosive, non-flammable and the largest volume inorganic chemical sold in the world. It is used in freezing foods, biological sample preservation and cryogenic therapy. Nitrogen may be found in DOT 4-L cylinders on city street corners used by electric and phone companies to keep underground conduits dry. However, this practice is diminishing.

Hydrogen—1:848. Liquid hydrogen is kept at extremely cold temperatures (-423 degrees Fahrenheit), can be found in laboratory settings and is used as rocket fuel and in hydrogen fuel cells. Its dangers include oxygen displacement, cold temperatures and high flammability. Hydrogen also burns with an invisible flame.

Carbon Dioxide—1:535. Carbon dioxide cannot be liquefied by just lowering its temperature; it also must be pressurized. This is why we say that CO₂ exists only as a gas or solid (dry ice). Once its temperature is lowered to less than -24 degrees Fahrenheit and pressurized, it becomes a liquid and has the same dangers as in its gaseous form. Though the temperature does not meet the definition of a cryogenic, it still is considered to be one. It is colorless, odorless, non-flammable and heavier than air. It is used in food preservation, fire extinguishers and the entertainment industry. It is used in most bar and restaurant soda systems.

change its state of matter from a liquid to a gas at 212 degrees Fahrenheit. Now think about cryogenic liquids with boiling points that start at -130 degrees Fahrenheit and go as low as -450 degrees Fahrenheit (the boiling point of helium). At these extreme temperatures, the leaking product condenses the moisture/humidity in the air, creating a highly visible vapor cloud. However, there are times when the leaking vapors will be invisible. This is dependent on the cylinder's location and rate of the leak.

Working with cryogenic materials is dangerous if one is not properly prepared. Special cryogenic gloves should be used when working with valves and piping and conducting mitigation efforts. Bare skin quickly will stick to metal components. Prolonged exposure easily will cause frostbite and solidification of body parts. The eyes are the most sensitive body part to the extreme cold.

3. **Pressure**—As we all know, propane has an expansion ratio of 270 to 1, which means that one gallon of liquid propane will yield 270 gallons of propane gas. This is why it is stored as a liquid; we get more in the cylinder. The same holds true for cryogenic-stored liquids, except the expansion ratios are much greater. Liquid nitrogen expands 1:696 times. Liquid hydrogen expands 1:848 times. When these gases expand and take the place of the oxygen, they not only cause an oxygen-deficient atmosphere, but increase the pressure in the room where the leak is located. Frequently, these tanks are stored in small rooms or closets. As the liquid leaks and vaporizes, the expanding gases quickly build up pressure in the area,

which has the potential to blow out doors and windows. Storage in lockers or cabinets can have the same effect. These conditions can cause injuries to responders.

Containers and Transportation

There are two main vessels that store cryogenic liquids. The first is the DOT 4L cryo-tank or cylinder (Photo 1). They are designed similarly to a thermos; a cylinder within a cylinder. The outer tank usually is constructed of stainless steel and contains all the

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valves, gauges and relief devices within a protective ring on top. This ring is useful as a handhold grip. The inner tank contains the actual product. The space between the two tanks contains insulation and is under vacuum pressure. Additionally, within the vacuum space, there is a copper tube that is coiled around the inner tank that contains product and is used to keep the inner vessel cold.

The tank may have either two or four hand valves. All valves should be marked with a small metal tag, identifying what the valve is. However, many times, they are not. When unmarked, it makes it very difficult to distinguish what is what. If it has two hand valves, one is the vent valve and the other is a liquid valve. If it contains four valves, it features a vent valve, liquid valve (which are always opposite each other), a gas valve

and pressure-building valve. Usually, on top of the cylinder in the middle of the tank is a liquid level gauge. Finally, the arm coming off the center of the tank that does not contain a hand valve is the pressure gauge, with a relief valve and a rupture disc. The relief

device is spring-loaded and set at 22, 230 or 350 psig. The rupture disc—aka burst disc—is designed to protect the inner tank (Photo 2).

The second vessel is known as a Dewar. Frequently, the DOT 4L is referred to as a Dewar, but, technically, this is incorrect. The 4L is a cylinder. A Dewar is a vacuum flask (Photo 3) and is a non-pressure container. These cryogenic Dewars come in various shapes and sizes (five to 200 liters) and are used to hold a specific cryogenic, usually for immediate use. They have double walls with a vacuum space in between these walls. They are designed to be open on the top or have a loose-fitting stopper. The smaller and simplest of these Dewars feature an opening on top with no plug negating pressure buildup.

Cryogenic material can be transported in the DOT 4L, similar to other low- and high-pressure cylinders, usually on a flatbed truck. Bulk transportation includes the MC 338. These trailers are particularly easy to spot on the highway, due to their rear compartment or cabinet that houses the pump and valves. Drivers of these rigs refer to these compartments as a “doghouse.” Members also may be familiar with the large cryogenic tanks found at hospitals and medical facilities. The same rules apply when responding to a leak.

Response Considerations

- When entering an area of a leaking or suspected leaking cylinder or Dewar, members should be wearing their SCBA and facepiece.
- Evacuate the building or area of all occupants until all potential dangers have been neutralized.
- Metering for oxygen concentration is of prime importance. Chief and company Officers should call for a unit that carries a multi-gas meter.
- Immediately call a Haz-Mat Technician Unit for advanced metering and mitigation capabilities.
- Ensure the response of an EMS Haz-Tac unit upon confirmation of a cryogenic leak.
- Consider the response of a Ventilation Support Unit.
- Fires involving liquefied cryogenics are colder than the water being applied to it for purposes of cooling and extinguishment. In reality, you actually are heating up the product, causing quicker expansion, which, in turn, may cause pressure buildup inside the tank. Any application of water during a fire should be used with extreme caution.
- With the product being extremely cold inside the tank, vaporization occurs through natural warming of the liquid. As it warms, it produces head pressure inside the cylinder. If the product is not used, it builds up enough pressure to activate the safety relief valve. This is a normal occurrence. As much as one to three percent of the product can be lost due to this process daily. This should be treated as a leak until it is confirmed otherwise by someone familiar with the cylinder.
- Never roll or drag a cylinder when trying to move it.
- When mitigating a leak or handling a leaking cylinder, use cryogenic gloves.
- Never randomly turn valves off or on and never attempt to plug the safety relief devices.
- Remember, liquefied cryogenics can have other associated dangers, such as toxicity (liquefied natural gas or LNG, carbon monoxide), flammability (hydrogen, methane, LNG) and oxidizers (oxygen).

Conclusion

Due to the physical properties and associated dangers of cryogenic liquid leaks, one must be properly informed and prepared



Photo 3—The Dewar is a non-pressure container.

when responding to such an incident. Officers should ensure that all members are properly geared up and prior to entering the building, wearing and using their SCBA. Too many things can go wrong due to the hidden dangers. Following these basic rules will facilitate a successful conclusion to any incident involving a cryogenic liquid. ■

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